

Restricted Metal-Arene and Phosphorus-Carbon Bond Rotation in (arene)Cr(CO)₂L Complexes (L = PPh₃, P(*o*-tolyl)₃)

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(1,4-Di-*tert*-butylbenzene)Cr(CO)₂PPh₃ exhibits restricted arene-Cr bond rotation in solution ($\Delta G^{\ddagger}_{203} = 31.6 \text{ kJ mol}^{-1}$). A series of (arene)Cr(CO)₂P(*o*-tolyl)₃ complexes have been prepared which exhibit restricted P-C rotation in solution; in cases where planar chirality is present, diastereoisomers may be observed which differ in the helicity of the exo₂ phosphine conformation. Diastereoisomer interconversion and *o*-tolyl ring exchange occur with very similar activation energies. Crystal structure data: (1,4-di-*tert*-butylbenzene)Cr(CO)₂PPh₃, monoclinic, space group $P2_1/n$, $a = 10.137(1) \text{ \AA}$, $b = 13.992(2) \text{ \AA}$, $c = 20.882(3) \text{ \AA}$, $\beta = 96.16(2)^\circ$, $Z = 4$, $R_w = 9.18\%$ for 345 refined parameters and 3643 observed reflections; (*p*-xylene)Cr(CO)₂P(*o*-tolyl)₃, monoclinic, space group $P2_1/n$, $a = 8.552(1) \text{ \AA}$, $b = 17.410(2) \text{ \AA}$, $c = 17.558(2) \text{ \AA}$, $\beta = 91.95(2)^\circ$, $Z = 4$, $R_w = 9.96\%$ for 317 defined parameters and 3392 observed reflections; (benzene)Cr(CO)₂P(*m*-tolyl)₃, monoclinic, space group $P2_1/n$, $a = 11.120(3) \text{ \AA}$, $b = 11.227(1) \text{ \AA}$, $c = 20.289(4) \text{ \AA}$, $\beta = 100.63(2)^\circ$, $Z = 4$, $R_w = 6.49\%$ for 299 defined parameters and 3127 observed reflections.

Introduction

There is now a general consensus that, in suitably substituted derivatives, barriers to metal-arene rotation in (arene)ML₃ complexes may be detected and measured using variable-temperature NMR spectroscopy. Such barriers may be electronic¹ or steric in origin, and with respect to the latter, work has concentrated mainly on hexasubstituted (C₆R₆)M(CO)₃ complexes (R = Et, Pr; M = Cr, Mo). Since the C_{3v} symmetry of the tricarbonyl precludes discrimination between C(arene)-R and arene-M rotation, desymmetrized complexes substituted at either the ring or the metal atom (but retaining the 1,3,5-distal, 2,4,6-proximal configuration of the ligand) have been used.² Barriers for C(arene)-R and arene-M rotation are in the ranges 28-49 and 28-40 kJ mol⁻¹, respectively, with the arene-M barrier being of lower energy in cases where they can be distinguished.³ Though substitution of CO by a more sterically demanding phosphine ligand might be expected to increase the barrier to arene-M rotation, in practice steric congestion is relieved by an increase in the distal/proximal ratio, and with the exceptions of 1^{2l,r} and the fused-ring complex 2,^{2m} arene-M rotation remains rapid on the NMR time scale at low

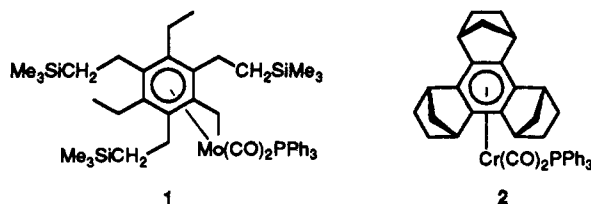
temperature.^{2a,b,e,f,h} Indeed, for simpler PPh₃ complexes, the process of highest energy is M-P rotation,⁴ with only two cases being reported in which restricted P-C rotation is also evident at low temperature.^{2l,r}

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(3) For examples of restricted C(arene)-X rotation in non-persubstituted complexes, see: (a) Mailvaganum, B.; Sayer, B. G.; McGlinchey, M. J. *J. Organomet. Chem.* 1990, 395, 177. (b) Van Meurs, F.; Baas, J. M. A.; van der Toorn, J. M.; van Bekkum, H. *J. Organomet. Chem.* 1976, 118, 305. (c) Campi, E. M.; Gatehouse, B. M. K.; Jackson, W. R.; Rae, I. D.; Wong, M. G. *Can. J. Chem.* 1984, 62, 2566. (d) Roques, B. P. *J. Organomet. Chem.* 1977, 136, 33.

* To whom correspondence should be addressed.

(1) (a) Acampora, M.; Ceccon, A.; Del Fara, M.; Giacometti, G.; Rigatti, G. *J. Chem. Soc., Perkin Trans. 2* 1977, 483. (b) Top, S.; Jaouen, G.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* 1983, 105, 6426. (c) Nambu, M.; Siegel, J. S. *J. Am. Chem. Soc.* 1988, 110, 3675. (d) Nambu, M.; Hardcastle, K.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* 1992, 114, 369.



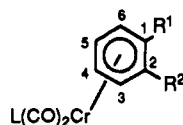
We wish to report here structural and stereodynamic studies on (*p*-Bu^t₂C₆H₄)Cr(CO)₂PPh₃ (**3e**), in which restricted metal–arene rotation may be observed as the process of highest energy, together with studies on the P(*o*-tolyl)₃ complexes in the series 3–5, in which P–C rotation may be identified as the process of highest energy. A crystal structure determination of the P(*m*-tolyl)₃ complex **3b** is also reported.

Results and Discussion

(a) Synthesis. Complexes in the series 3–5 were prepared photolytically from the tricarbonyl via the intermediacy of the (arene)Cr(CO)₂(cyclooctene) complex.⁵ For PPh₃, yields are better than direct photolysis, while direct photolysis of P(*o*-tolyl)₃ results in competitive P–C bond homolysis to give (*o*-tolyl)₂PP(*o*-tolyl)₂ and complexes thereof.⁶



- 3a: R¹ = R² = H; L = P(*o*-tolyl)₃ 4a: R¹ = R² = Me; L = P(*o*-tolyl)₃
 3b: R¹ = R² = H; L = P(*m*-tolyl)₃ 4b: R¹ = R² = Me; L = PPh₃
 3c: R¹ = R² = H; L = PPh₃ 4c: R¹ = R² = CO₂Me; L = P(*o*-tolyl)₃
 3d: R¹ = R² = Me; L = P(*o*-tolyl)₃ 4d: R¹ = R² = CO₂Me; L = PPh₃
 3e: R¹ = R² = Bu^t; L = PPh₃ 4e: R¹ = Me; R² = CO₂Me; L = P(*o*-tolyl)₃
 4f: R¹ = Me; R² = CO₂Me; L = PPh₃



- 5a: R¹ = Me; R² = CO₂Me; L = P(*o*-tolyl)₃
 5b: R¹ = Me; R² = CO₂Me; L = PPh₃

(b) Metal–Arene Rotation. Restricted metal–arene rotation in **3e** is evident in the collapse and resolution into two peaks of the single room-temperature ¹³C NMR resonance assigned to carbons 2, 3, 5, and 6 (Figure 1). All other carbon resonances (including the PPh₃ subspectrum) and the ³¹P resonance are temperature-independent and are consistent with population only of conformer A. Line-

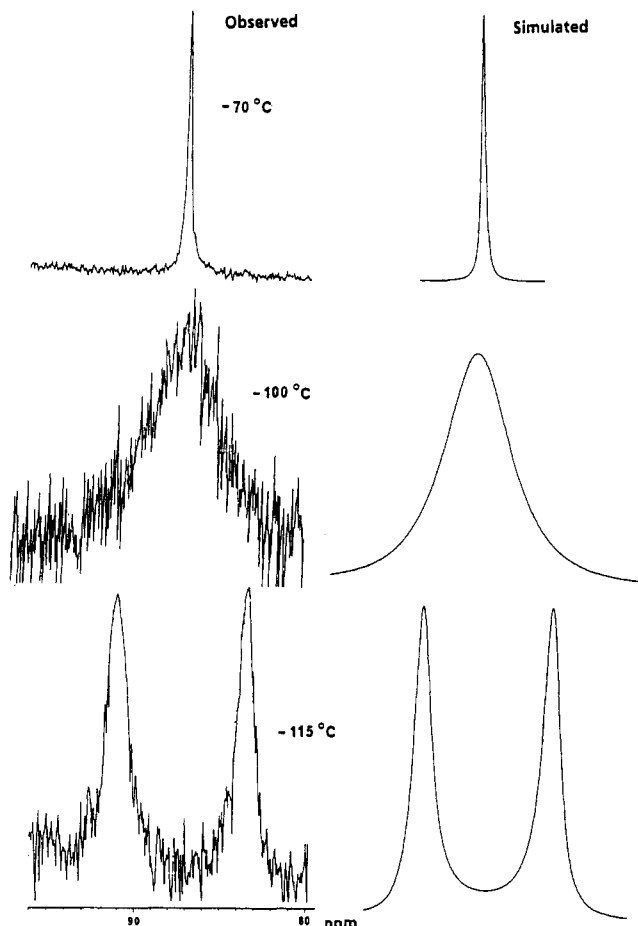
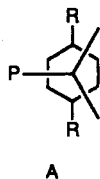


Figure 1. ¹³C NMR spectra for **3e**.

shape analysis (Figure 1, Table I) yields a ΔG^*_{203} value of 31.6 kJ mol⁻¹, which may be compared to ΔG^*_{298} values of 53–57 kJ mol⁻¹ for arene rotation in related (*p*-di-*tert*-butylbenzene)M(CO)(ER₃)₂ derivatives (M = Ru, Os; E = Si, Ge; R = Cl, Me).⁷ The NMR spectra of (*p*-di-*tert*-butylbenzene)Cr(CO)₃ are independent of temperature down to -110 °C.

A crystal structure determination has confirmed the conformation of **3e** (Figure 2, Table II). Relative to other PPh₃ complexes,⁸ the most important structural features are an elongated Cr–P bond, a contraction of the CO–M–CO angle at the expense of increasing one Z–Cr–CO angle, and a “boatlike” conformation of the arene in which (C₁C₄) and the Bu^t carbons lie above the (C₂C₃C₅C₆) plane by 0.07 and 0.35 Å, respectively.⁹ The orientation of the arene relative to Cr(CO)₂L is staggered (average $\angle$ L–Cr–Z–C(arene) = 30°), as expected for para disubstitution by electron-donating groups.¹⁰ The phosphine occupies the position farthest from the *tert*-butyl substituents.

(c) Phosphorus–Carbon Rotation. The NMR spectra of the PPh₃ complexes **3c**, **4b,d,f**, and **5b** are temperature-invariant down to -110 °C, thus indicating that metal–arene, metal–phosphorus, and phosphorus–carbon bond

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(8) For a survey of (arene)Cr(CO)₂PPh₃ complex geometries, see ref 2m.

(9) For similar observations, see: (a) Einstein, F. W. B.; Jones, T. *Inorg. Chem.* **1982**, *21*, 987. (b) Van Meurs, F.; van Koningsveld, H. *J. Organomet. Chem.* **1974**, *78*, 229.

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Table I. Kinetic and Activation Parameters

process	<i>T</i> (K)	<i>k</i> (s ⁻¹)	$\Delta G^\ddagger$ (kJ mol ⁻¹)
arene rotation in 3e	158	220	30.9
	173	1800	31.0
	188	9500	31.2
	203	35000	31.6
ring exchange in 3a	238	45	50.2
	248	120	50.4
	258	300	50.6
	273	1050	50.8
	283	2200	51.0
	298	6900	51.0
ring exchange in 4a	218 ^a	3	50.8
	228	9	51.1
	238	30	51.1
	248	120	50.4
	258	400	50.0
	268	900	50.2
	278	1500	51.0
	218 ^b	3	50.8
	228	9	51.1
	238	45	50.3
	248	120	50.4
	258	390	50.0
ring exchange/diastereoisomer interconversion in 5a	223 ^a	3	52.0
	243	18	53.2
	263	150	53.1
	283	1800	51.5
	223 ^b	3	52.0
	243	18	53.2
ring exchange/diastereoisomer interconversion in 4e	263 ^a	50	55.5
	283	800	53.4
	303	900	57.1
	223 ^b	10.5	49.7
	243	21	52.9
	263	360	51.2
	283	1800	51.5
	303	5400	52.5

^a From line-shape analysis of π -arene methyl resonances. ^b From line-shape analysis of *o*-tolyl methyl resonances.

rotations remain fast on the NMR time scale. These results are consistent with those of Hunter et al.,^{4a} which show that Cr-P rotation remains fast as long as two adjacent positions on the benzene ring are unsubstituted.

In contrast, the ¹H and ¹³C spectra of **3a** reveal a decoalescence of both methyl and arene resonances of the P(*o*-tolyl)₃ ligand. Neither the π -arene nor the ³¹P resonances change with temperature. These results are most consistent with hindered rotation of the P-C_{ipso} bonds in an *exo*₂ conformation,¹¹ while both metal-arene and metal-phosphorus rotation remain rapid. Line-shape analysis of the proton ortho methyl resonance (Figure 3, Table I) yields a $\Delta G^\ddagger_{238}$ value of 50.2 kJ mol⁻¹, considerably higher than analogous processes in Cr(CO)₅P(*o*-tolyl)₃ and Fe(CO)₄P(*o*-tolyl)₃ ($\Delta G^\ddagger_{233}$ = 38.6 and 44.6 kJ mol⁻¹, respectively).¹² Studies on the *p*-xylene complex confirm this interpretation; in addition to changes in the P(*o*-tolyl)₃ subspectrum, the two-line ¹³C *p*-xylene room-temperature

(11) If a regular trigonal pyramid is constructed with the metal as apex and the three para ring carbons as the base, a proximal (*exo*) substituent will point away from the base while a distal (*endo*) substituent will point toward the base. The term *exo*₂ defines the number of proximal ortho methyl groups.

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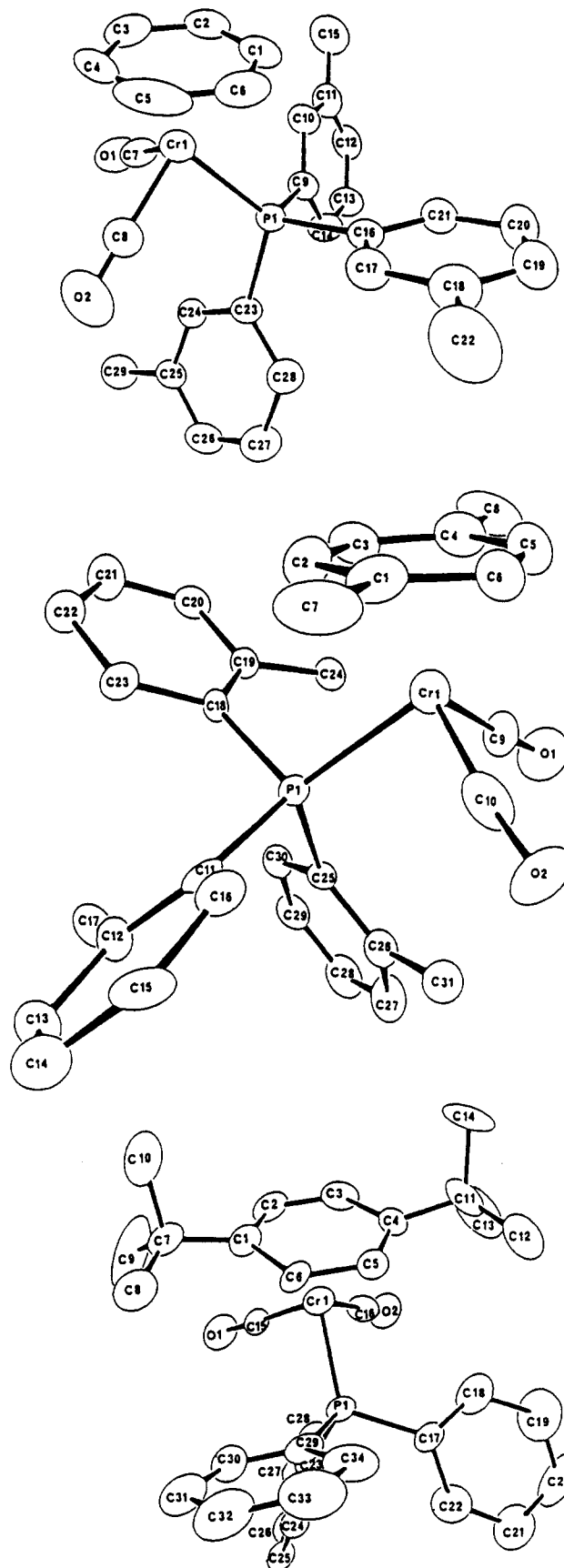


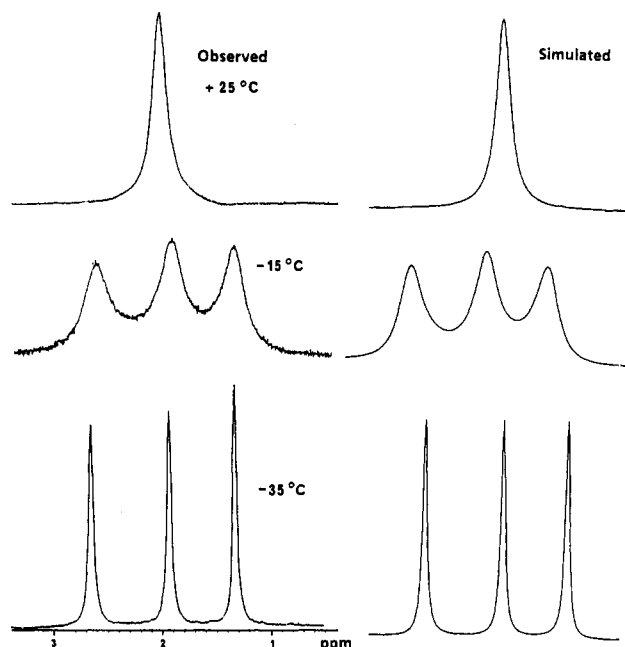
Figure 2. Molecular structures of **3b** (top), **3d** (middle), and **3e** (bottom).

spectrum is resolved into three lines at low temperature (Table III). The temperature independence of C₁ and C₄ and the methyl resonance shows that arene-metal rotation remains rapid on the NMR time scale at low temperature.

Table II. Important Structural Parameters for 3b,d,e

	3b	3d	3e
Cr-P	2.32	2.40	2.33
Cr-Z ^b	1.70	1.72	1.70
Cr-CO (av)	1.83	1.83	1.81
C-O (av)	1.16	1.16	1.17
C-C(ring) (av)	1.38	1.41	1.42
P-C (av)	1.84	1.86	1.84
∠Z-Cr-CO	124.9	121.2	124.5
	126.8	125.9	131.7
∠Z-Cr-P	128.0	126.5	126.9
∠CO-Cr-CO	87.9	88.0	82.9
∠CO-Cr-P	87.6	91.0	89.5
	88.8	95.0	91.5
∠C-P-C (av)	101.9	102.6	100.4
∠Cr-P-C(ipso)-C(ortho)	32	57	35
	51	70	44
	56	-6	79

^a Distances are in angstroms and angles in degrees. ^b Z is the centroid of the π -arene ring.

Figure 3. ¹H NMR spectra for 3a.

In complexes 3a,d and 4a,c, slowing of P-C rotation is accompanied by transformation of the single phosphorus-coupled room-temperature ¹³CO resonance into a diastereotopic pair at low temperature.

A crystal structure determination of 3d (Figure 2, Table II) confirms the *exo*₂ conformation of the phosphine. In common with 3e, an elongated Cr-P bond and a compressed CO-M-CO angle are observed. The boatlike configuration is much reduced in character, with (C₁C₄) and the methyl carbons lying 0.02 and 0.10 Å, respectively, from the (C₂C₃C₅C₆) plane. These results are consistent with recent studies on 1,4-disubstituted complexes containing nonsterically demanding π -donor groups.¹³ The Cr(CO)₂L moiety is slightly displaced from the staggered configuration (average $\angle$ L-Cr-Z-C(arene) = 19, 32°). The plane of the distal ring of the *exo*₂ phosphine is essentially collinear with the Cr-P axis.

NMR spectra of the P(*m*-tolyl)₃ complex 3b are temperature-independent. Though P-C rotational barriers are undoubtedly lower compared to those of 3a, the C₃

Table III. Summary of Variable-Temperature ¹³C Spectra of P(*o*-tolyl)₃ Complexes^a

compd	signal type	high temp (20 °C)	low temp (-65 to -85 °C)
3a	1-6	89.8	n
	<i>o</i> -tolyl	22.7	24.1 [17], 22.8, 22.4 [5]
3d	CO	241.0 [22]	243.7 [18], 240.4 [17]
	2,3,5,6	90.9 (br)	89.2, 92.5
4a	1,4	102.8	n
	Me	19.0	n
	<i>o</i> -tolyl	22.9 (br)	22.9, 23.1, 24.9
	CO	242.6 (br)	241.4 [16], 244.7 [16]
	1,3	103.5 (br)	102.4, 103.8
	4,6	90.7 (br)	89.8, 92.7
	2,5	86.3, 97.6	n
	Me	19.5	20.0, 20.4
	<i>o</i> -tolyl	23.0 (br)	23.0 [5], 23.3, 25.0 [5]
	CO	242.0 (br)	244.6 [17], 241.3 [17]
4c	1,3	not detected	76.9, 84.6
	4,6	99.0 (br)	91.3, 100.5
	2,5	90.7, 91.0	n
	CO ₂ Me	52.3, 167.1	52.2, 166.5
			52.5, 166.5
	<i>o</i> -tolyl	23.5 (br)	22.6 [5], 23.1, 25.4 [3]
	CO	not detected	237.5 [18], 238.6 [17]
	1	not detected	104.7, 97.1
	3	87.6 (br)	79.6, 85.5
	2,4-6	93.0 (br), 91.2	97.8, 91.7
5a			97.2, 91.4
			92.5, 90.9
	Me	19.3	91.8, 86.3
	CO ₂ Me	52.1, 168.0	19.4, 19.6
			52.0, 168.9
	<i>o</i> -tolyl	22.8 (br)	51.7, 167.5
			22.4, 22.8
	CO	240.3 (br)	24.2, 25.0
			241.6 [16], 241.2 [16]
			239.1 [16], 239.7 [16]
5a	1	not detected	106.8, 102.3
	2	not detected	79.6, 82.2
	3-6	90.5 (br), 93.5	88.4, 94.6
			91.9, 97.1
			93.6
	Me	20.1	21.1, 21.4
	CO ₂ Me	51.9, CO ₂ Me	51.7, 167.6
		not detected	52.1, 168.6
	<i>o</i> -tolyl	22.7 (br)	22.5, 22.8
			24.2, 24.9
5a	CO	239.9 (br)	241.4 [18], 241.1 [18]
			239.2 [18], 238.9 [18]

^a The letter n indicates no change with temperature. Some resonances were not detected at room temperature due to extreme broadness. Chemical shifts are given in ppm; *J* values in Hz are given in brackets.

*exo*₃ symmetry of the phosphine (Figure 2, Table II) precludes investigation in any case. Spectra of P(*m*-tolyl)₃ and SP(*m*-tolyl)₃ are similarly temperature-independent,¹⁴ though the solid-state structures are *exo*₂ and *exo*₁, respectively.¹⁵ The orientation of the Cr(CO)₂L moiety relative to the ring is intermediate between staggered and eclipsed (average $\angle$ L-Cr-Z-C(arene) = 15, 45°); (benzene)-Cr(CO)₃ has the staggered structure¹⁶ predicted on electronic grounds,¹⁰ but one may note the small energy difference between staggered and eclipsed forms of phosphine-substituted derivatives of (C₆Et₆)Cr(CO)₃.^{2b,f}

These structures provide an interesting comparison in terms of cone angle of the phosphine.¹⁷ Thus, for both 3b and 3e, the cone angle is determined by the van der Waals

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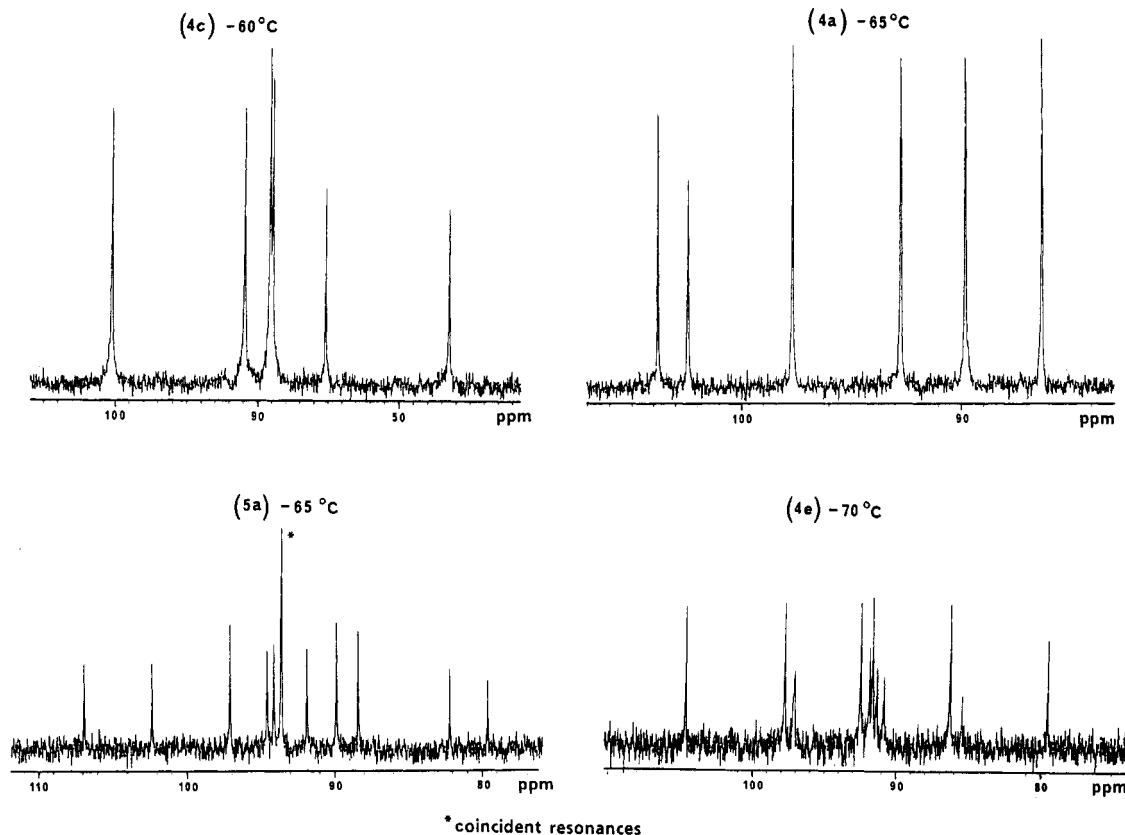


Figure 4. Low-temperature ^{13}C NMR spectra for 4a,c,e and 5a.

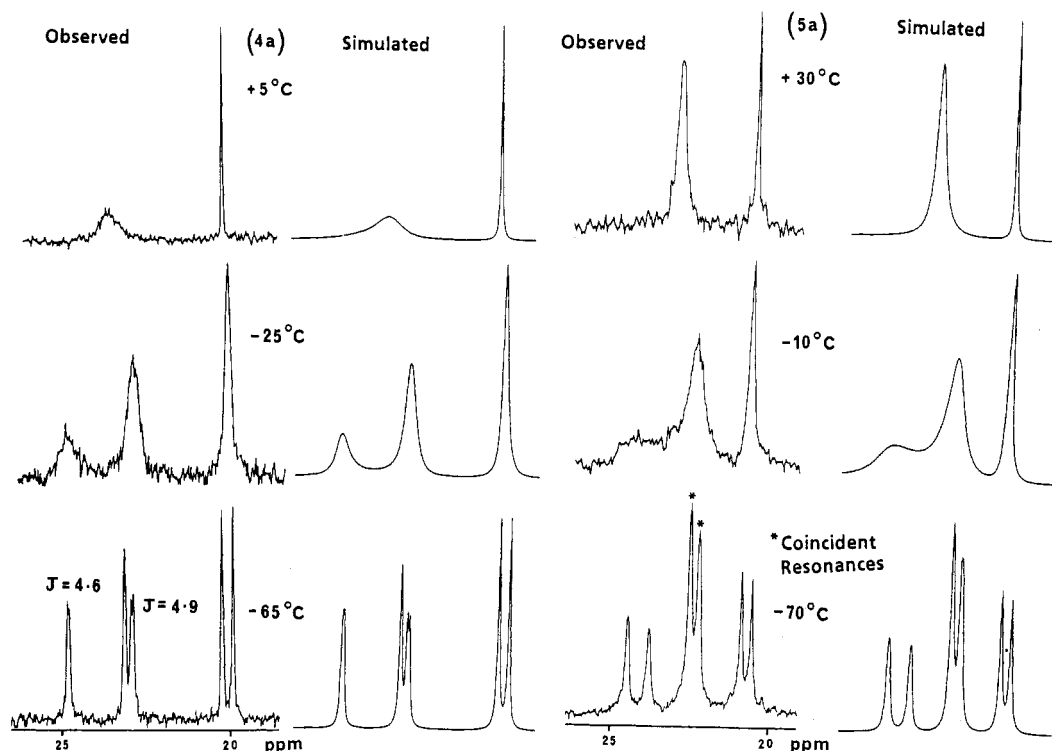


Figure 5. ^{13}C NMR spectra for 4a and 5a.

interaction of the ortho hydrogen, and both are equal to 145° , the accepted literature value. In contrast, the cone angle in 3d is 160° , substantially less than the literature value of 194° based on an exo_3 conformation. Thus, in 3d, intramolecular repulsions between the phosphine and

other ligands are minimized at the expense of an increase in intraphosphine interactions; molecular mechanics calculations on the free phosphine indicate that the exo_3 conformation is more stable than the exo_2 by approximately 9 kJ mol^{-1} .¹⁴

For asymmetrically substituted complexes such as 4e and 5a, diastereoisomers are possible which differ only in the screw sense of the phosphine helix relative to the planar

(17) Calculated by CHEM-X using van der Waals radii of 1.2 and 2.0 Å, respectively, for hydrogen and the methyl group: CHEM-X, designed and distributed by Chemical Design Limited, Oxford, England.

Table IV. Crystallographic Data

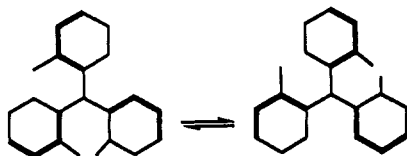
	3d	3e	3b
space group	monoclinic	monoclinic	monoclinic
<i>a</i> , Å	<i>P</i> 2 ₁ / <i>n</i> 8.552(1)	<i>P</i> 2 ₁ / <i>n</i> 10.137(1)	<i>P</i> 2 ₁ / <i>n</i> 11.120(3)
<i>b</i> , Å	17.410(2)	13.992(2)	11.227(1)
<i>c</i> , Å	17.558(2)	20.882(3)	20.289(4)
β, deg	91.95(2)	96.16(2)	100.63(2)
<i>V</i> , Å ³	2612	2945	2489
<i>Z</i>	4	4	4
<i>F</i> (000)	1096	1192	1024
2θ range, deg	2 < 2θ < 119	2 < 2θ < 52	2 < 2θ < 60
reflms with <i>I</i> > 3σ(<i>I</i>)	3392	3643	3127
variable params	317	345	299
max shift/esd	<0.001	<0.002	<0.001
max excursion, e/Å ³	0.45	0.67	0.17
min excursion, e/Å ³	-0.36	-0.67	-0.20
<i>R</i> , %	8.88	9.87	5.82
<i>R</i> _w , %	9.96	9.18	6.49

chirality. Such interactions are thought to be vital in determining the relative stabilities of diastereoisomeric intermediates in catalytic asymmetric hydrogenation,¹⁸ while the synthetically useful CpFe(CO)(PPh₃)COR series exhibits a correlation between the screw sense of the phosphine helix and the configuration at the metal center.¹⁹

Thus, the ¹³C π-arene subspectra of 4e and 5a are resolved into 12 resonances at low temperature (Figure 4), together with a doubling of CO, CO₂Me, and ³¹P resonances (Table III). In CD₂Cl₂, the diastereoisomer ratios for 5a and 4e are approximately 1:1 and 2:1, respectively; these ratios decrease to 0.8:1 and 1:1 in toluene-*d*₈. The possibility that such multiplicity is the result of some restricted conformational process involving metal-arene, metal-phosphorus, or C(arene)-CO₂Me rotation is unlikely; the symmetrical complexes 4a,c exhibit only six-line π-arene subspectra at low temperature (Figure 4).

The mechanisms of ring exchange in triarylphosphines via correlated ring rotation have been extensively analyzed by Mislow and co-workers.²⁰ For the asymmetrically substituted complexes 4e and 5a, two processes may potentially be distinguished, as follows.

(i) A three-ring flip in the exo₂ conformation may occur



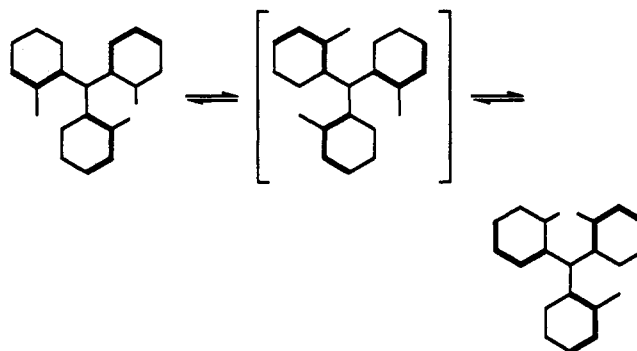
which results in helix interconversion and exchanges the two proximal *o*-tolyl rings but retains the identity of the distal ring.

In achiral derivatives such as 3a and 4a, such a mechanism should result in preferential collapse of two *o*-tolyl methyl resonances, a process which is not observed. Similar studies of ring exchange in (CO)₅CrP(*o*-tolyl)₃¹² and the XP(*o*-tolyl)₃ series (X = S, Se)¹⁴ also show an equivalent collapse of the *o*-tolyl subspectrum. Thus, the intermediacy of this mechanism seems unlikely, even though it provides a direct pathway for diastereoisomer exchange via helix inversion.

Table V. Fractional Atomic Coordinates for 3b

atom	<i>x</i>	<i>y</i>	<i>z</i>
Cr(1)	0.89308(6)	0.42550(6)	0.14050(4)
P(1)	1.04258(9)	0.28967(9)	0.18557(5)
O(1)	0.9089(5)	0.3293(4)	0.0054(2)
O(2)	0.7028(4)	0.2421(4)	0.1505(3)
C(1)	1.0039(5)	0.5731(4)	0.1909(3)
C(2)	0.9783(6)	0.5986(4)	0.1253(3)
C(3)	0.8572(7)	0.5953(5)	0.0901(3)
C(4)	0.7632(6)	0.5709(5)	0.1250(5)
C(5)	0.7932(9)	0.5488(5)	0.1941(5)
C(6)	0.9156(8)	0.5502(5)	0.2271(3)
C(7)	0.9030(5)	0.3656(4)	0.0581(2)
C(8)	0.7774(5)	0.3120(4)	0.1462(3)
C(9)	1.1824(3)	0.2825(4)	0.1490(2)
C(10)	1.2243(4)	0.3860(4)	0.1230(2)
C(11)	1.3331(4)	0.3872(5)	0.0976(2)
C(12)	1.396(4)	0.2837(5)	0.0978(2)
C(13)	1.3576(5)	0.1797(5)	0.1226(3)
C(14)	1.2490(4)	0.1784(4)	0.1485(2)
C(15)	1.3777(5)	0.5021(6)	0.0722(3)
C(16)	1.1031(4)	0.3067(3)	0.2751(2)
C(17)	1.0206(4)	0.3140(4)	0.3190(2)
C(18)	1.0574(5)	0.3308(4)	0.3873(2)
C(19)	1.1801(5)	0.3410(5)	0.4125(2)
C(20)	1.2657(5)	0.3353(5)	0.3705(3)
C(21)	1.2275(4)	0.3182(4)	0.3023(2)
C(22)	0.9638(7)	0.3390(7)	0.4324(3)
C(23)	0.9954(4)	0.1318(3)	0.1798(2)
C(24)	0.9477(4)	0.0859(4)	0.1167(2)
C(25)	0.9072(4)	-0.0316(4)	0.1077(2)
C(26)	0.9138(4)	-0.1024(4)	0.1642(3)
C(27)	0.9643(5)	-0.0596(4)	0.2271(3)
C(28)	1.0063(4)	0.0571(4)	0.2348(2)
C(29)	0.8583(6)	-0.0797(4)	0.0383(3)

(ii) A two-ring flip mechanism, in which ring exchange occurs via an exo₃ intermediate, may occur:



For 4a, the expected equivalent collapse of the *o*-tolyl subspectrum is observed, and as the two prochiral methyl groups are interconverted only by complete *o*-tolyl ring exchange, line-shape analyses (Figure 5) of both *o*-tolyl and xylyl resonances yield identical activation parameters within the precision of the measurements. For a chiral complex, the two-ring flip without helix inversion of the exo₃ intermediate should result in a simplification of the *o*-tolyl subspectrum from six resonances to two but retain two arene-methyl resonances, since diastereoisomeric integrity is preserved. If, however, the barrier to helix inversion via a three-ring flip in the exo₃ intermediate is small or comparable to the barrier for the two-ring flip in the ground-state exo₂ configuration, an equivalent collapse of all resonances will be expected. For 5a, line-shape analysis indeed yields identical parameters for *o*-tolyl and arene methyl exchange. For 4e, the small chemical shift difference between the arene methyl resonances provides a rather narrow range of temperatures over which interconversion can be measured with good precision. Nev-

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Table VI. Fractional Atomic Coordinates for 3d

atom	x	y	z
Cr(1)	0.16063(8)	0.39059(4)	0.34626(4)
P(1)	0.13960(12)	0.36498(6)	0.21196(6)
O(1)	0.5006(5)	0.4260(3)	0.3332(3)
O(2)	0.2439(5)	0.2330(2)	0.3972(2)
C(1)	-0.0713(6)	0.3775(3)	0.4020(3)
C(2)	-0.0866(6)	0.4315(3)	0.3433(3)
C(3)	0.0131(6)	0.4961(3)	0.3414(3)
C(4)	0.1281(7)	0.5078(3)	0.3955(3)
C(5)	0.1478(6)	0.4526(3)	0.4530(3)
C(6)	0.0534(7)	0.3888(3)	0.4568(3)
C(7)	-0.1827(7)	0.3115(4)	0.4088(4)
C(8)	0.2341(9)	0.5765(4)	0.3974(4)
C(9)	0.3666(6)	0.4122(3)	0.3369(3)
C(10)	0.2154(6)	0.2923(3)	0.3727(2)
C(11)	0.0251(5)	0.2785(2)	0.1823(2)
C(12)	-0.0060(5)	0.2538(2)	0.1059(2)
C(13)	-0.0836(5)	0.1834(3)	0.0946(3)
C(14)	-0.1291(6)	0.1383(3)	0.1537(4)
C(15)	-0.1006(6)	0.1631(3)	0.2277(3)
C(16)	-0.0261(5)	0.2312(3)	0.2398(3)
C(17)	0.0375(6)	0.2967(3)	0.0364(3)
C(18)	0.0359(5)	0.4468(2)	0.1657(2)
C(19)	0.1002(5)	0.5194(2)	0.1595(2)
C(20)	0.0043(6)	0.5789(3)	0.1312(3)
C(21)	-0.1487(6)	0.5686(3)	0.1122(3)
C(22)	-0.2149(6)	0.4965(3)	0.1215(3)
C(23)	-0.1236(5)	0.4360(3)	0.1465(3)
C(24)	0.2671(6)	0.5416(3)	0.1826(3)
C(25)	0.3152(5)	0.3506(2)	0.1526(2)
C(26)	0.4256(5)	0.2946(3)	0.1691(3)
C(27)	0.5510(6)	0.2850(3)	0.1200(3)
C(28)	0.5673(5)	0.3307(3)	0.0556(3)
C(29)	0.4566(7)	0.3833(3)	0.0389(3)
C(30)	0.3302(6)	0.3951(3)	0.0865(3)
C(31)	0.4206(6)	0.2428(3)	0.2372(3)

ertheless, above 250 K, these resonances appear to exchange more slowly than the *o*-tolyl resonances, suggesting that the three-ring flip process in the exo_3 intermediate can be distinguished as the process of highest energy. It may be noted that molecular mechanics studies of free $\text{P}(\text{o-tolyl})_3$ reveal almost identical energies for the idealized transition state of the two-ring flip and the transition state of the three-ring flip for the exo_3 conformer. Transition states for direct helix interconversion in the exo_2 conformation lie at much higher energies.

Experimental Section

NMR spectra were recorded using a JEOL GSX270 spectrometer; temperatures were measured using the built-in copper-constantan thermocouple. Line-shape analyses were performed using the EXCHANGE program (R. E. D. McClung, University of Alberta). $\text{P}(\text{o-tolyl})_3$ ²¹ and $(\text{arene})\text{Cr}(\text{CO})_3$ complexes²² were prepared by standard methods.

(a) Synthesis. A representative synthesis of $(\text{benzene})\text{Cr}(\text{CO})_2\text{P}(\text{o-tolyl})_3$ (**3a**) is given below; other compounds were prepared by the same method.

$(\text{Benzene})\text{Cr}(\text{CO})_3$ (2 g, 9 mmol) was dissolved in a mixture of *cis*-cyclooctene (45 mL) and toluene (215 mL) and was irradiated for 1.5 h using a 90-W medium-pressure mercury lamp. $\text{P}(\text{o-tolyl})_3$ (2.8 g, 9 mmol) was added and the mixture stirred in the dark for 30 min. After filtration through Celite and removal of solvent, the crude product was purified by chromatography on grade IV alumina using 10% ethyl acetate/90% petroleum ether (40–60 °C). After elution of small amounts of the faster moving tricarbonyl, the product **3a** (2.8 g, 63%) was eluted and recrystallized from ethyl acetate. Anal. Calcd for $\text{C}_{29}\text{H}_{27}\text{O}_2\text{CrP}$: C, 71.0; H, 5.55. Found: C, 71.0; H, 5.67. Mp: 175 °C dec. Infrared

Table VII. Fractional Atomic Coordinates for 3e

atom	x	y	z
Cr(1)	0.07798(11)	0.89163(8)	0.19374(6)
P(1)	-0.0187(2)	0.7577(1)	0.1418(1)
O(1)	0.2161(7)	0.9443(4)	0.0796(3)
O(2)	0.3282(6)	0.7816(4)	0.2282(3)
C(1)	-0.0413(8)	1.0322(5)	0.1877(4)
C(2)	0.0821(9)	1.0415(6)	0.2209(4)
C(3)	0.1251(8)	0.9859(6)	0.2774(4)
C(4)	0.0398(8)	0.9147(6)	0.2995(3)
C(5)	-0.0789(7)	0.8990(5)	0.2606(3)
C(6)	-0.1216(8)	0.9560(5)	0.2042(4)
C(7)	-0.0902(10)	1.1058(6)	0.1373(4)
C(8)	-0.2234(15)	1.0797(7)	0.1008(6)
C(9)	0.0020(15)	1.1263(9)	0.0905(8)
C(10)	-0.1169(12)	1.1973(7)	0.1723(6)
C(11)	0.0706(10)	0.8707(8)	0.3647(4)
C(12)	-0.0273(11)	0.7909(8)	0.3779(4)
C(13)	0.2127(12)	0.8302(11)	0.3740(5)
C(14)	0.0590(16)	0.9485(10)	0.4128(6)
C(15)	0.1603(8)	0.9225(5)	0.1244(4)
C(16)	0.2291(8)	0.8228(6)	0.2153(4)
C(17)	-0.0289(9)	0.6453(5)	0.1869(4)
C(18)	0.0420(9)	0.6370(6)	0.2462(6)
C(19)	0.0437(10)	0.5519(9)	0.2820(6)
C(20)	-0.0278(12)	0.4758(7)	0.2556(7)
C(21)	-0.1015(15)	0.4837(7)	0.1947(6)
C(22)	-0.1002(13)	0.5678(7)	0.1642(5)
C(23)	0.0548(7)	0.7061(5)	0.0712(4)
C(24)	-0.0181(8)	0.6582(5)	0.0217(3)
C(25)	0.0448(9)	0.6137(6)	-0.0252(4)
C(26)	0.1789(9)	0.6149(6)	-0.0226(4)
C(27)	0.2523(8)	0.6632(6)	0.0234(4)
C(28)	0.1943(8)	0.7076(6)	0.0731(4)
C(29)	-0.1903(8)	0.7765(6)	0.1091(4)
C(30)	-0.2185(9)	0.8288(6)	0.0518(4)
C(31)	-0.3459(11)	0.8553(7)	0.0267(6)
C(32)	-0.4486(11)	0.8253(9)	0.0613(8)
C(33)	-0.4227(10)	0.7753(10)	0.1190(7)
C(34)	-0.2975(8)	0.7489(7)	0.1417(5)

(hexane): 1907, 1859 cm^{-1} . NMR: ^1H , 4.58 [2] (1–6), 2.0 (br, *o*-tolyl); ^{31}P , 89.6.

Other Complexes. **3b**: 60% yield. Anal. Calcd for $\text{C}_{29}\text{H}_{27}\text{O}_2\text{CrP}$: C, 71.0; H, 5.55. Found: C, 71.1; H, 5.45. Mp: 138–140 °C. Infrared (CH_2Cl_2): 1883, 1827 cm^{-1} . NMR: ^{13}C , 90.1 (1–6), 21.3 (*m*-tolyl), 241.0 [22] (CO); ^1H , 4.26 [2] (1–6), 2.31 (*m*-tolyl); ^{31}P , 90.1.

3c: 48% yield. Anal. Calcd for $\text{C}_{28}\text{H}_{21}\text{O}_2\text{CrP}$: C, 69.6; H, 4.69. Found: C, 69.5; H, 4.73. Mp: 199–201 °C. Infrared (hexane): 1915, 1859 cm^{-1} . NMR: ^{13}C , 89.7 (1–6), 240.6 [22] (CO); ^1H , 4.26 [2] (1–6); ^{31}P , 91.1.

3d: 69% yield. Anal. Calcd for $\text{C}_{31}\text{H}_{31}\text{O}_2\text{CrP}$: C, 71.8; H, 6.03. Found: C, 71.7; H, 6.00. Mp: 163 °C dec. Infrared (CH_2Cl_2): 1871, 1815 cm^{-1} . NMR: ^1H , 3.97 (br, 2, 3, 5, 6), 1.87 (Me), 2.25 (br, *o*-tolyl); ^{31}P , 92.3.

3e: 62% yield. Anal. Calcd for $\text{C}_{34}\text{H}_{37}\text{O}_2\text{CrP}$: C, 72.8; H, 6.65. Found: C, 72.6; H, 6.45. Mp: 217–221 °C dec. Infrared (CH_2Cl_2): 1871, 1807 cm^{-1} . NMR: ^{13}C , 122.1 (1,4), 86.6 (2,3,5,6), 30.6, 33.8 (Bu^t), 241.7 [20] (CO); ^1H , 4.48 [2] (2,3,5,7), 1.09 (Bu^t); ^{31}P , 89.1.

4a: 44% yield. Anal. Calcd for $\text{C}_{31}\text{H}_{31}\text{O}_2\text{CrP}$: C, 71.8; H, 6.03. Found: C, 71.7; H, 6.30. Mp: 162 °C dec. Infrared (CH_2Cl_2): 1895, 1842 cm^{-1} . NMR: ^1H , 4.13 (br, 4,6), 3.57 [6] (5), 3.99 (2), 1.99 (Me), 2.23 (br, *o*-tolyl); ^{31}P , 92.6.

4b: 58% yield. Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{O}_2\text{CrP}$: C, 70.6; H, 5.29. Found: C, 70.7; H, 5.41. Mp: 177–178 °C. Infrared (CH_2Cl_2): 1895, 1847 cm^{-1} . NMR: ^{13}C , 105.0 (1,3), 89.9 (4,6), 86.3, 93.8 (2,5), 20.2 (Me), 241.3 [20] (CO); ^1H , 3.93 (4,6), 4.29 [6] (5), 4.11 (2), 1.93 (Me); ^{31}P , 93.0.

4c: 37% yield. Anal. Calcd for $\text{C}_{33}\text{H}_{31}\text{O}_6\text{CrP}$: C, 65.3; H, 5.83. Found: C, 65.6; H, 5.24. Mp: 153 °C dec. Infrared (CH_2Cl_2): 1915, 1867 cm^{-1} . NMR: ^1H , 5.4 (br, 4, 6), 6.91 (2), 3.78 (5), 3.38 (CO_2Me), 2.10 (br, *o*-tolyl); ^{31}P , 81.5.

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4d: 65% yield. Anal. Calcd for C₃₀H₂₅O₆CrP: C, 63.8; H, 4.46. Found: C, 64.0; H, 4.43. Mp: 156–157 °C. Infrared (CH₂-Cl₂): 1923, 1871 cm⁻¹. NMR: ¹³C, 83.3 (1,3), 94.3 (4,6), 85.7, 90.5 (2,5), 52.4, 166.6 (CO₂Me), 236.9 [21] (CO); ¹H, 5.53 [1] (4,6), 6.80 (2), 3.96 [3] (5); ³¹P, 82.4.

4e: 51% yield. Anal. Calcd for C₃₂H₃₁O₄CrP: C, 68.3; H, 5.55. Found: C, 68.3; H, 5.51. Mp: 136 °C dec. Infrared (CH₂-Cl₂): 1907, 1863 cm⁻¹. NMR: ¹H, 5.56 (br, 2), 5.25 (br, 4), 4.34 (br, 5, 6), 1.90 (br, Me), 3.48 (CO₂Me), 2.15 (br, *o*-tolyl); ³¹P, 86.0.

5a: 45% yield. Anal. Calcd for C₃₂H₃₁O₄CrP: C, 68.3; H, 5.55. Found: C, 68.6; H, 5.24. Mp: 160–161 °C. Infrared (CH₂-Cl₂): 1915, 1867 cm⁻¹. NMR: ¹H, 5.31 (br, 3), 3.95, 4.15 (br, 4–6), 2.57 (Me), 3.36 (CO₂Me), 2.05 (br, *o*-tolyl); ³¹P, 87.0.

NMR spectral data²³ for **4f**: ¹³C, 102.4 (1), 86.0 (3), 92.7, 90.9, 90.5, 88.1 (2,4–6), 20.3 (Me), 52.1, 168.7 (CO₂Me), 239.5 [21], 239.3 [21] (CO); ¹H, 5.56 (2), 5.46 (4), 4.31 (5,6), 3.34 (CO₂Me), 1.41 (Me); ³¹P, 87.8.

NMR spectral data²³ for **5b**: ¹³C, 105.7 (1), 83.0 (2), 94.0, 93.1, 90.9, 87.3 (3–6), 21.4 (Me), 51.7, 168.2 (CO₂Me), 239.1 [21], 238.6 [21] (CO); ¹H, 5.69 (3), 4.40 (5), 4.06 (4), 3.94 (6), 2.60 (Me), 3.33 (CO₂Me); ³¹P, 87.9.

¹³C NMR chemical shifts (CD₂Cl₂ solution) and ¹H NMR chemical shifts (C₆D₆ solution) are given in ppm relative to TMS; ³¹P chemical shifts (CD₂Cl₂ solution) are relative to 85% H₃PO₄. Coupling constants *J*(P–C) and *J*(P–H) are in brackets (in units of Hz); *J*(H–H) values are in the range 6.5–7.0 Hz (ortho) and 1.5–2.0 Hz (meta). Aryl ¹³C and ¹H resonances of the phosphine ligands are seen between 128 and 143 and between 6.6 and 8.9 ppm, respectively. The ³¹P resonances of **4e** and **5a** are resolved into two lines at low temperature.

(b) X-ray Crystallography. Data were collected on an Enraf-Nonius CAD4F diffractometer using Mo K α radiation for

3d and **3b** (λ = 0.7107 Å) and Cu K α radiation (λ = 1.541 84 Å) for **3e**. The structures were solved by direct methods (SHELX86)²⁴ and refined by full-matrix least squares (SHELX76).²⁵ Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atoms were included at calculated positions with fixed thermal parameters; non-hydrogen atoms were refined anisotropically. Atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.^{26–28} All calculations were performed on a VAX 8700 computer. Atomic coordinates are listed in Tables V–VII.

The high *R* values for **3d** and **3e** are due to poorer crystal quality. In the case of **3e**, correction for absorption did not improve the quality of the results, and a careful search for disorder in the *tert*-butyl groups did not reveal any extra peaks.

Supplementary Material Available: Tables of crystal data and data collection and refinement details, bond distances and angles, hydrogen atom positional parameters, and anisotropic thermal parameters and additional drawings of **3b,d,e** (31 pages). Ordering information is given on any current masthead page.

OM920756+

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